REPORT DOCUMENTATION PAGE

AFRL-SR-AR-TR-03-

0284

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
		01 SEP 2002 - 31 MAY 2003 Final Report

4. TITLE AND SUBTITLE
(STTR PHASE 1) Controlled Nucleation and Growth in Semiconductor Epitaxy

5. FUNDING NUMBERS
65502F
STTR/TX

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ARLINGTON VA 22203

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
F49620-02-C-0091

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION AVAILABILITY STATEMENT
APPROVED FOR PUBLIC RELEASE, DISTRIBUTION UNLIMITED

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

During Phase I support two types of ultrasonic transducers were designed and fabricated. These transducers were utilized for ultrasonically assisted deposition of silicon under Molecular Beam Epitaxy (MBE). Epitaxial Si growth on (100) Si wafers has been observed at reduced substrate heater temperatures when accompanied by simultaneous ultrasonic agitation of the substrate during deposition.

20030731 105

14. SUBJECT TERMS			15. NUMBER OF PAGES
			16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

Controlled Nucleation and Growth in Semiconductor Epitaxy

Final Report

June 30, 2003

1. Introduction

Thermal budget is the most significant factor in the growth process of high quality epitaxial structures. Basically, substrate temperature is utilized to promote surface mobility during growth, preventing "pile-ups", and allowing the arriving atoms to position themselves in the optimal sites. There are many processes or device structures however, that cannot survive highly elevated temperatures. In addition, when the substrate is at very high temperatures, the energy content is sufficient to generate a variety of defects. Therefore, a reduction of the thermal budget during the growth process while still maintaining the quality of the epitaxial film could bring great many benefits to device fabrication.

In this work, ultrasonic agitation is been utilized to promote surface atomic mobility during silicon deposition, and to allow for a reduced thermal budget in the epitaxial growth process. This deposition scheme may also prove beneficial for a reduction of the thermal budget in the fabrication process of "difficult" materials such as SiC, diamond, and GaN, as well as for the production of materials with a significantly reduced defect density. In addition, it may allow for novel methods that cannot be considered at elevated temperatures, to be incorporated in the fabrication process.

Our silicon/adsorbed oxygen superlattice (Si/O superlattice) was introduced as an epitaxial barrier for silicon quantum devices. This structure forms the basis for an epitaxially grown insulating layer on a silicon wafer, which can have significant technological implications as a replacement of the traditional SOI (Silicon on Insulator). In addition, stable electroluminescence in the visible region has been observed from an epitaxial Si/O superlattice.[1,2] Although we have already achieved low defect densities of less than 10^9 /cm^2 for the epitaxial Si/O superlattice, further reduction in the defects by using ultrasound would greatly benefit many novel applications such as silicon-based quantum devices, three dimensional integrated circuits, etc. Recently, our company and Prof. R. Tsu of UNC-Charlotte, also introduced a novel approach for fabricating Si/C superlattices, which can be used as wide bandgap materials mimicking many of the properties of SiC, but also as a template for CVD growth of SiC. Both of these structures can make particularly good use of epi-CVD deposition if a reduced thermal budget can be applied by the use of ultrasound, in order to retain the in situ oxygen layer without surface evaporation or ion migration in the crystal structure initiated by elevated temperatures. Our ultrasonically assisted deposition technique may also benefit the CVD heteroepitaxy of diamond, at reduced temperature and improved crystallinity.

Phase I dealt with the identification of appropriate materials for the implementation of ultrasonic transducers suitable for the demanding environment of MBE and CVD deposition systems, the design and fabrication of such transducers, and the investigation of the ultrasonically assisted deposition technique in the growth of epitaxial silicon layers and superlattices. A reduction in the required substrate temperature for epitaxial silicon growth of up to 30% has been demonstrated under Phase I.

2. Identification of appropriate materials for the construction of piezoelectric transducers to be used in Ultra High Vacuum Environment

Several piezoelectric materials are commercially available for manufacturing transducers. In modern transducers, most commonly used are polycrystalline piezoelectric ceramics, such as lead zirconate titanate (PZT), lead titanate, barium titanate, lead metaniobate, bismuth titanate, etc. However, some single crystalline materials, such as quartz and lithium niobate ($LiNbO_3$), also possess piezoelectric properties and can be considered for manufacturing ultrasonic transducers.

In order to be suitable for use in ultrasonically assisted deposition of semiconductor devices, the chosen material must satisfy several quite challenging requirements. In Molecular Beam Epitaxial (MBE) growth for example, the base pressure typically approaches 10^{-10} Torr. Therefore, the chosen piezoelectric material should be suitable for use in ultra high vacuum environment. In addition, during the Si/O superlattice fabrication process, the first step after the silicon substrate is introduced in the growth chamber, involves heating the wafer to 850 °C, at 10^{-10} Torr. An alternative approach would be to expose the silicon surface at much lower temperatures in a reducing atmosphere (perhaps forming gas H_2/N_2, 10%/90%), to remove any surface oxides. This provides a clean surface for further growth. Even if the 850 °C step is omitted, we still need to be able to go to temperatures of up to 350 - 400 °C for silicon deposition, even after a 25-30% reduction of silicon growth temperature with the help of the ultrasound. In addition, materials such as SiC require even higher temperature, and in the CVD process substrate temperature cannot be reduced to a level below what is required for the thermal decomposition of the source vapor molecules. Thus, the chosen piezoelectric material should be able to withstand high temperatures. Finally, the material should be able to withstand these high temperatures without outgasing, which would destroy the epitaxy and possibly even contaminate our growth chamber. Recapitulating, our chosen materials for the ultrasonic transducer, should satisfy the following important requirements:

- Be suitable for use in ultra high vacuum environment.
- Be able to withstand high temperature, at least up to 400 °C, but preferably up to 850 °C.
- Should not outgas at high temperature.

The above-mentioned requirements severely limited our choice of available materials. Most transducers using ceramic piezoelectrics, are designed to operate at temperatures less than 100 °C. We found only a few ceramic piezoelectric materials that could

withstand higher temperatures. A modified lead metaniobate ceramic, available from the Keramos division of Piezo Technologies Inc. [3], under the product name Kezite K81, and from Boston Piezo-Optics Inc. [4], under the product code VP-M18, has a Curie temperature of 400 °C, and it is specified for operation up to 300 °C. This temperature however is still lower than our minimum requirement. We found one more candidate ceramic material from Piezo Technologies Inc, (Keramos division) with the commercial name Kezite K15. This ceramic is based on modified bismuth titanate. It has a Curie temperature higher than 600 °C, and it is advertised for high temperature applications, up to 500 °C. Having some concerns about introducing a material composed of bismuth in our MBE system, we discussed with the vendor (Piezo Technologies) the stability of this ceramic at higher temperatures, and found that it may undergo chemical reduction at temperatures above 350 °C, releasing oxygen. Since this would contaminate our system and destroy the epitaxy, Kezite K15 was eliminated from our selection list. However, as the manufacturer is developing a modified version of this material with improved stability, K15 may remain an option for future experiments in Phase II.

Having difficulties in identifying ceramic piezoelectric products suitable for our application, we turned our focus to single-crystal piezoelectric materials. Quartz is relatively inexpensive and rather easy to manufacture, therefore it was our first choice. However, having a Curie temperature of 573 °C, it will probably be only marginally suitable for our application at 400 - 500 °C; and it cannot be used for our process at 850°C. Lithium Niobate ($LiNbO_3$) has a Curie point of 1150 °C, and therefore it is well within the range of our temperature requirements. In addition, the $LiNbO_3$ crystal can provide stronger ultrasonic agitation than the Quartz crystal. Lithium Niobate single crystal though, is quite expensive and rather difficult to manufacture, especially for larger diameter crystals. We purchased several lithium niobate and quartz single crystals at several diameters and for various resonance frequencies from Boston Piezo-Optics Inc. The crystals are round in shape (disks) with diameters ranging from 0.375" to 1.5", and thickness from 0.072" to 0.136". Their resonance frequency is between 1.0 MHz and 1.5 MHz. All crystals are polished, and have vacuum deposited gold / chrome electrodes, 3500 - 5000 Å thick, on both surfaces.

3. Design of the Piezoelectric Transducer

The piezoelectric transducers were designed with the primary goal to deliver as much ultrasonic power to the substrate as possible. For this purpose, a very good physical contact between the piezoelectric crystal and the wafer is essential, in particular since the growth process takes place under high vacuum conditions.

Figure 1 shows two designs for ultrasonic transducers for two different piezoelectric crystal sizes. In the first configuration, the piezoelectric crystal and the semiconductor wafer are sandwiched between two molybdenum disks, 2.8" in diameter, designed to fit onto the growth stage. The two molybdenum disks provide the top and bottom electrical contacts to the piezoelectric crystal. They are held together with stainless steel screws, and they are electrically isolated from each other by means of ceramic "hats" (see Fig. 1(b)). When the whole structure is positioned onto the growth stage with the help of our

magnetic transfer mechanism, the bottom disk snaps onto the growth stage cup, providing the ground contact. The top disk is designed to snap onto a stainless steel fixture positioned on the growth stage, but electrically isolated from it.

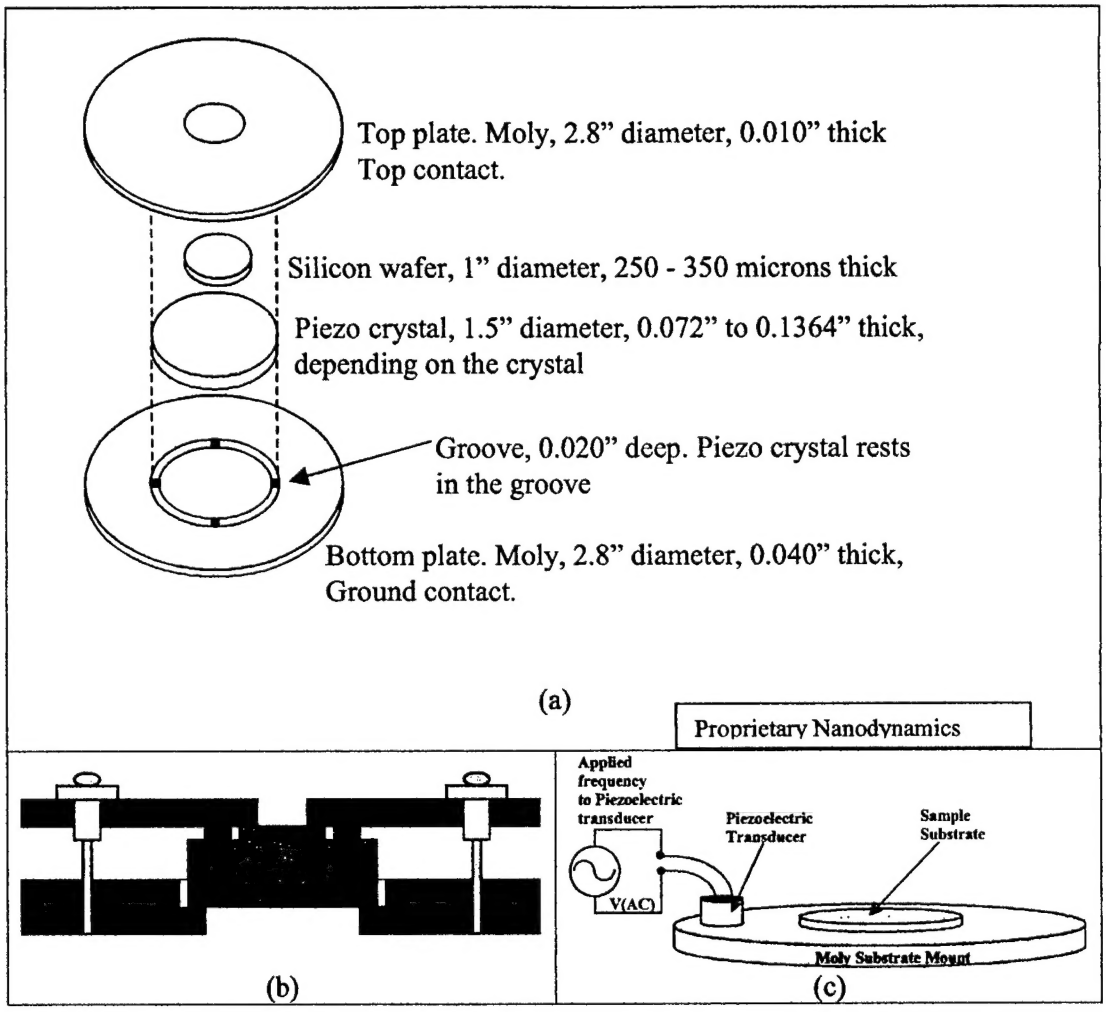
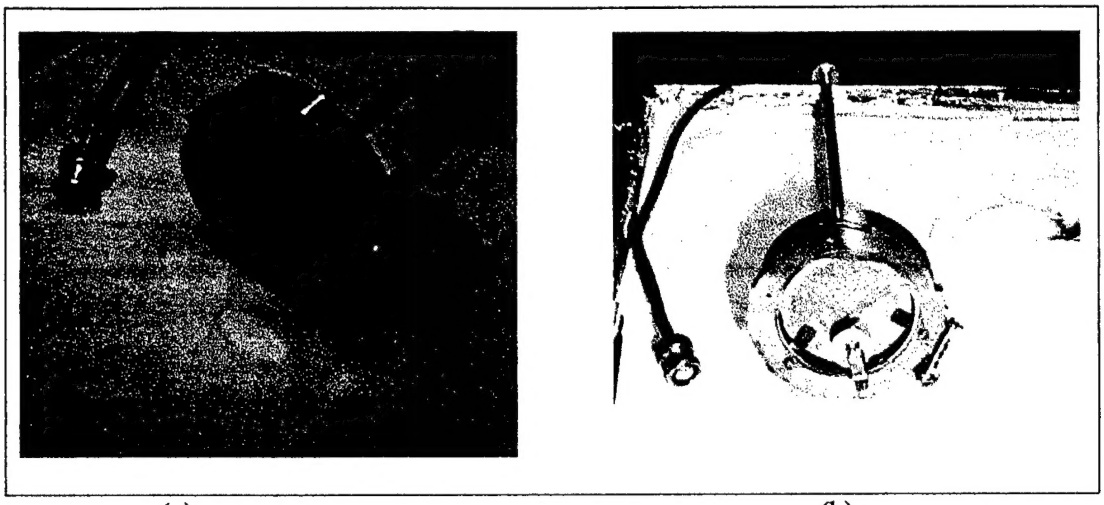


Fig. 1. Schematic of the piezoelectric transducer used in our MBE silicon deposition experiments; (a) expanded view of the transducer utilized to accommodate 1.5" piezoelectric crystals and 1" silicon wafers; (b) Cross sectional view of the same transducer design; (c) schematic view of the transducer designed for smaller diameter piezoelectric crystals.

A molybdenum wire attached to a BNC electrical feedthrough provides the other contact. The second transducer configuration, shown schematically in Fig. 1(c), is designed to accommodate smaller diameter (0.3" to 0.5") piezoelectric crystals. A spring-loaded stainless steel "hat" is utilized to support the piezoelectric crystal and to provide firm contact with the semiconductor wafer. Two molybdenum rings provide the frame of the structure (see Fig. 2b below). The electrical contacts and the positioning of the transducer

onto the growth stage are made in a quite similar manner as described above for the large size transducer.



(a) (b)

Fig. 2. Photographs of the two transducers with $LiNbO_3$ crystals, taken after they were removed from the vacuum system. (a) Transducer for 1.5" diameter piezoelectric crystals. (b) Transducer for 0.3" - 0.5" diameter crystals

Proprietary Nanodynamics

Based on the above designs, two ultrasonic transducers that can accommodate either quartz or $LiNbO_3$ piezoelectric crystals were fabricated by Nanodynamics. Both transducers have been utilized in our experiments. Photographs of the two transducers incorporating $LiNbO_3$ crystals and silicon wafers, taken after they were removed from the vacuum system, are shown in Fig. 2. For deposition utilizing the small transducers, a thin layer of gold/chrome was sputtered on the silicon wafer, covering about 1/3 of its surface. This layer served as the bottom contact of the ultrasonic transducer.

Another important issue for the successful implementation of the ultrasonically assisted deposition experiments is the coupling between the components of the ultrasonic transducer, to maximize energy transfer between the piezoelectric crystal and the silicon wafer. The best way to transfer energy would be through coupling via a solid or fluid medium [5]. In most experiments we used indium as a coupling medium. Indium will melt at elevated temperatures providing fluid coupling. Indium will not destroy the epitaxy; however, care must be taken during its placement on the transducer, so that the molten indium will not cause any electrical shorts. This method with indium as the coupling medium worked quite well in our experiments. Some experiments were also carried out with "dry coupling", where the ultrasonic transducer's components are coupled by high pressure. To facilitate better coupling, a polished piezoelectric crystal and a double side polished silicon wafer were used. Although this method is simpler, we encountered some problems with energy transfer and with the electrical contacts. Some

initial experiments with "dry coupling" resulted in the cracking of the piezoelectric crystal. Most of the subsequent experiments were carried out with indium coupling.

Both quartz and $LiNbO_3$ piezoelectric crystals were used in our experiments. Both materials are suitable for use in ultra high vacuum environment. However, after the initial experiments, single crystalline lithium niobate ($LiNbO_3$) materials have been selected as the preferred piezoelectric elements for the construction of the transducers, mainly because they offer strong piezoelectric properties and have a high Curie point of 1150 °C.

The ultrasonic transducer is driven by an AG1006 low frequency generator/amplifier manufactured by T&C Power Conversion, Inc [6]. The AG1006 can provide continuous wave excitation at the resonant frequencies of our crystals. It is a class "B" generator/amplifier, operating at variable frequencies from 20 kHz to 10 MHz. An impedance matching circuit is used between the driver and the oscillator. The AG1006 can be computer controlled by a menu driven software. The computer connection is via an RS-232 port. Figure 3 shows a block diagram of the configuration of the instruments used in our experiment.

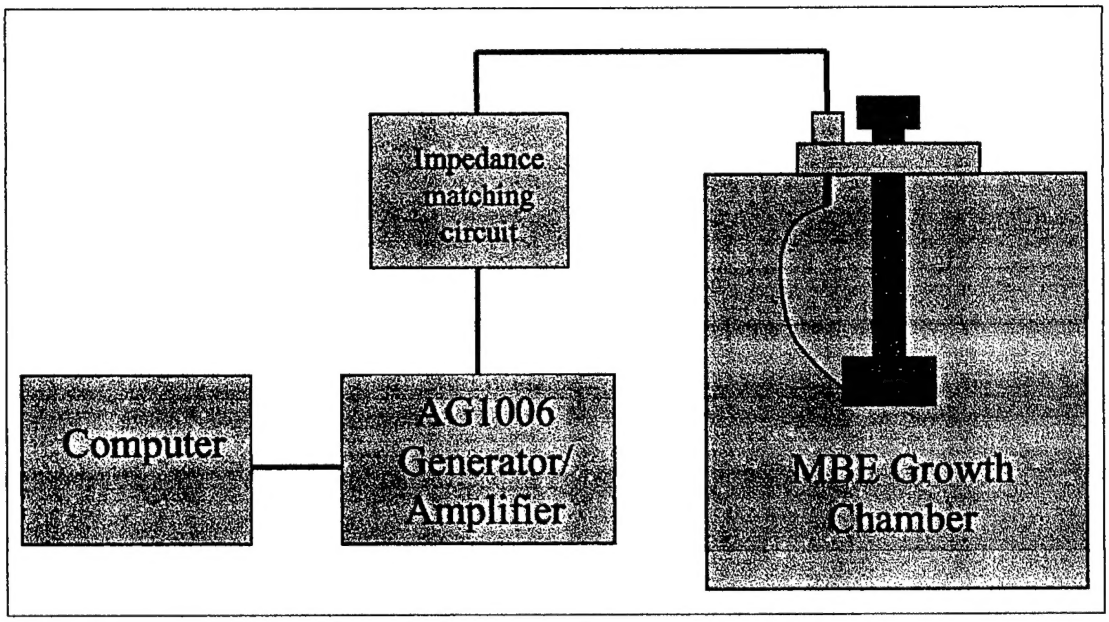


Fig. 3. Block diagram of the instrumentation used in our ultrasound enhanced deposition experiment.

Proprietary Nanodynamics

4. Experimental procedures and results

Details of the experimental procedures and results of ultrasonically assisted silicon deposition follow. A transducer utilizing a 1.5" diameter lithium niobate ($LiNbO_3$) crystal

in contact with a (100) silicon wafer was assembled, according to the configuration shown in Fig. 1. The thickness of the $LiNbO_3$ crystal is 0.14" and its resonance frequency 1 MHz. A thin indium foil is placed between the $LiNbO_3$ crystal and the silicon wafer to facilitate better energy coupling. Thin pieces of indium are also placed at the contact points between the $LiNbO_3$ crystal and the molybdenum structure, to improve electrical and mechanical connections. The silicon wafer is degreased using standard procedures, followed by immersion in dilute aqueous hydrofluoric acid (HF) solution to remove the native oxide and to facilitate hydrogen terminated surface. As soon as this step is completed, the transducer is assembled and loaded into the growth chamber as quickly as possible. After the structure is moved into the growth chamber the wafer is heated to facilitate a clean silicon surface. The ultrasonic transducer is controlled via a computer interface as shown in Fig. 3, and the impedance matching circuitry is optimized to deliver maximum power to the load. The frequency of the generator signal is tuned until it exactly matches the resonance frequency of the piezoelectric crystal and maximum power is delivered to the crystal under resonance. Fig. 4 shows a picture of the user interface on the computer screen utilized to control the transducer. In Fig. 5, the total, reflected and load powers are plotted versus time. Note that under optimized conditions about 95% of the generator power is deliver to the load and the reflected power is very small. Also, the same figure shows the stability of the system during operation.

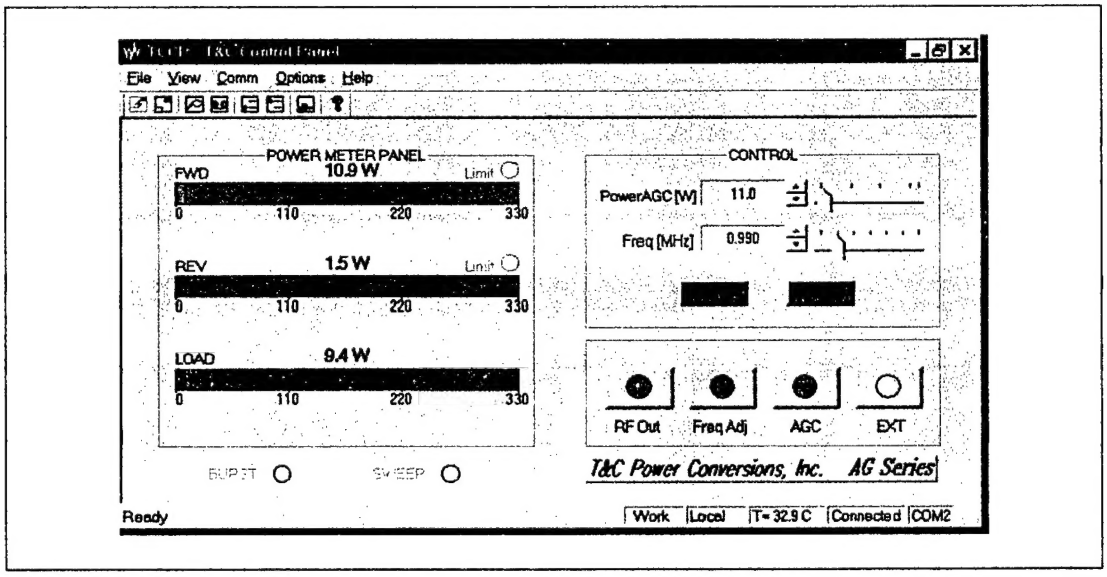


Fig. 4. Graphical User Interface of the software used to control the ultrasonic transducer during the deposition experiments.

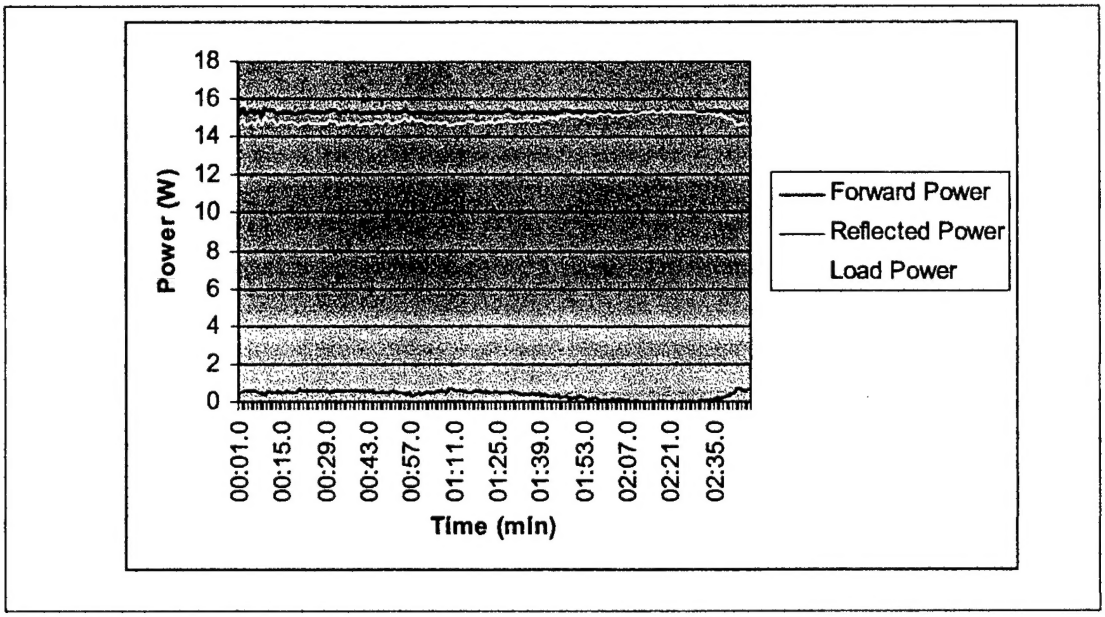


Fig. 5. Load power to the ultrasonic transducer vs. time, showing excellent power transfer and stability.

Proprietary Nanodynamics

In situ Reflection High Energy Electron Diffraction (RHEED) is utilized to monitor the quality of the epitaxy. The RHEED pattern of the silicon substrate at 450 °C and 600 °C is shown in Figs. 6 (a) and 6 (b) respectively. Note that at 600 °C the half order is still not clear yet, indicating a surface not perfectly reconstructed. Nevertheless, we decided to proceed with the epitaxial growth. 300 Å of silicon were deposited at a substrate temperature of 600 °C, and at a rate of 0.5 Å/sec, with the oscillator "off". The RHEED pattern after this step is shown in Fig. 6 (c). Note that the half order is almost lost, and that the lines shown in the previous RHEED pattern (6 b), are transformed into "dots" indicating a three-dimensional structure (3D pattern). At this point the oscillator was turned "on" at low power. Then 100 Å of silicon were deposited at the same temperature (600 °C) and at the same rate (0.5 Å/sec). The resulted RHEED pattern is shown in Fig. 6 (d). Note that the "half order" (labeled on Fig. 6) is now recovered, and the "dots" elongated, indicating a transformation from a 3D pattern to a two-dimensional (2D) pattern. This indicates an improvement in the epitaxial structure, with deposition under ultrasonic assistance.

At this point the ultrasonic oscillator was turned "off", and an additional 100 Å of silicon was deposited at 600 °C and 0.5 Å/sec. Fig. 7 (a) shows the resulting RHEED pattern. A good 2D pattern is observed indicating excellent epitaxy even with the oscillator off, since the surface has been improved from the preceding growth. Turning the ultrasound "on", and depositing 100 Å of silicon at the same temperature of 600 °C and a rate of 0.5 Å/sec., results in an improved 2D pattern with more pronounced half order lines, as shown in Fig. 7 (b).

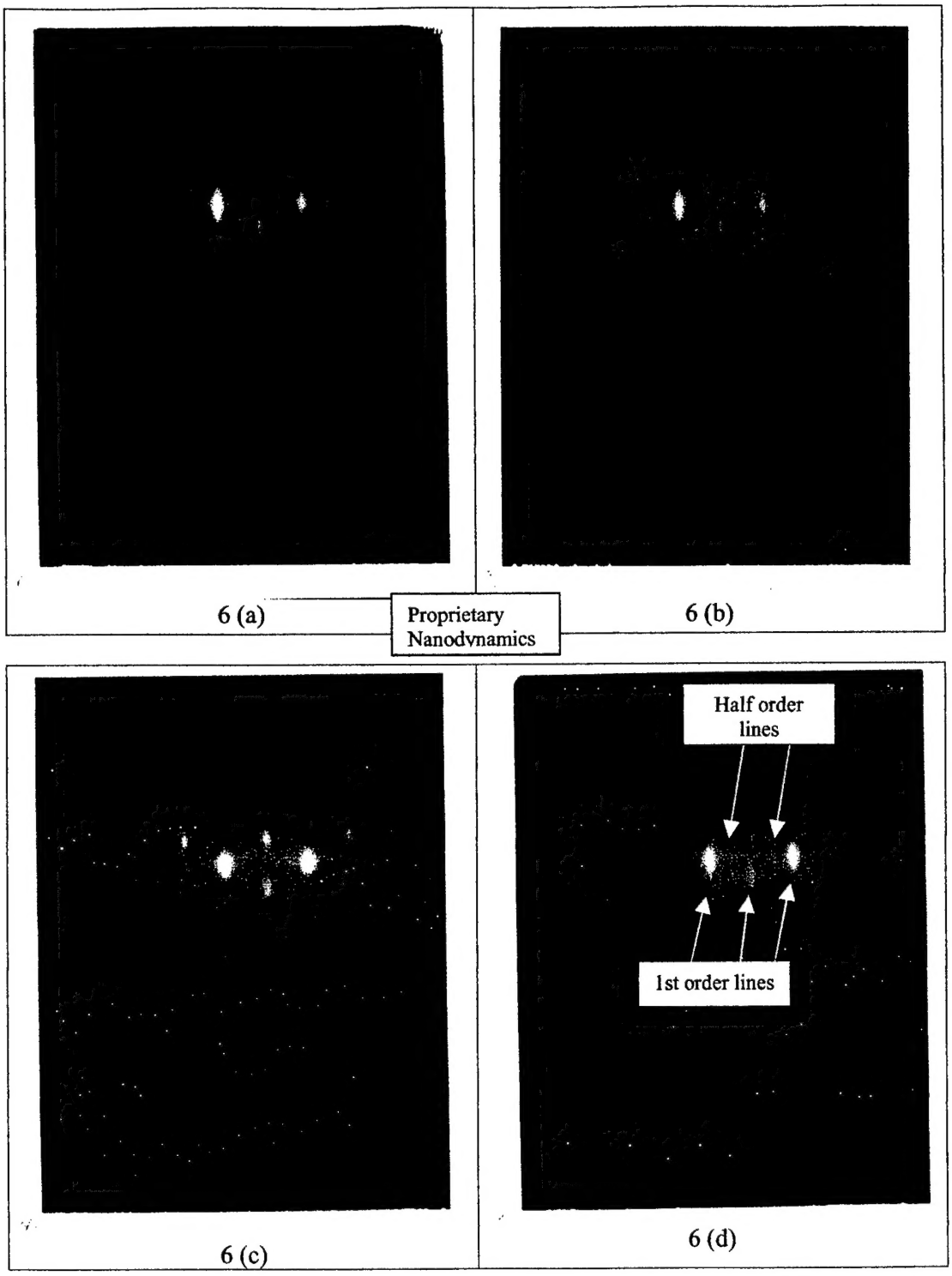


Fig. 6. (a,b) RHEED pattern of the silicon substrate at (a) 450°C, and (b) 600 °C. (c) After deposition of 300 Å of silicon at 600 °C, and 0.5 Å/sec, with the oscillator "off". (d) After additional 100 Å of silicon at 600 °C, and 0.5 Å/sec, with the oscillator "on".

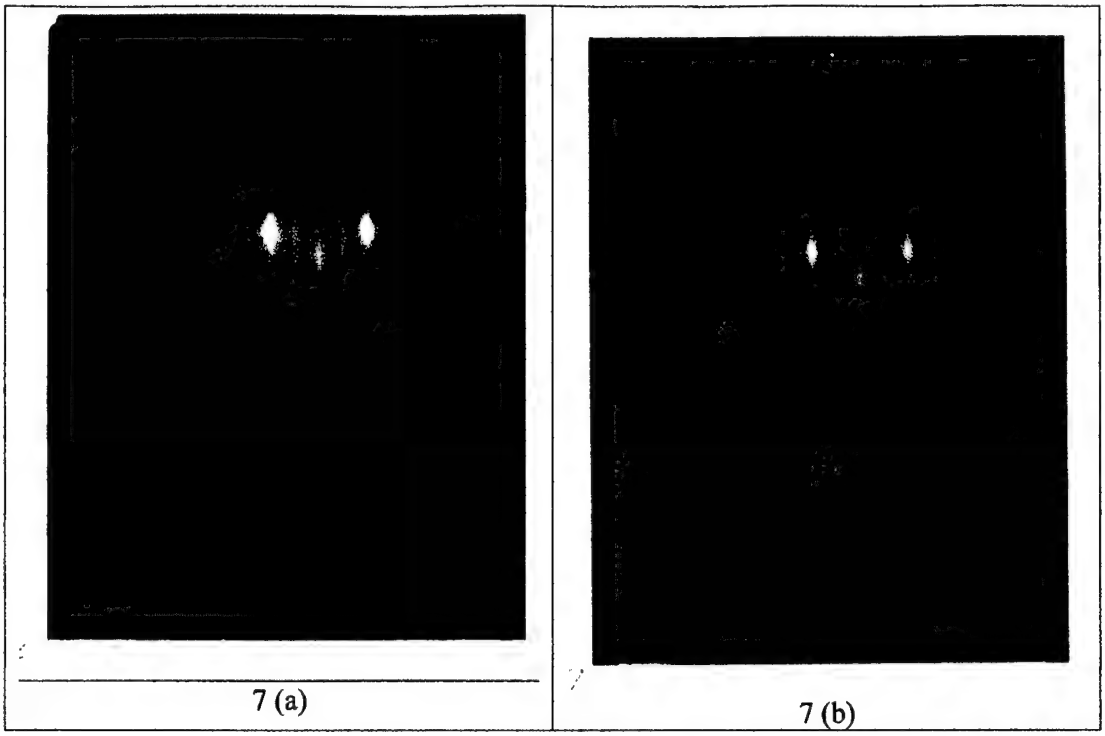


Fig. 7. (a) Additional 100 Å of silicon at 600 °C, and 0.5 Å/sec, with the oscillator "off". (b) Additional 100 Å of silicon at 600 °C, and 0.5 Å/sec, with the oscillator "on".

Proprietary Nanodynamics

We have shown that deposition assisted by an ultrasonic field results in an improvement in the epitaxial structure, even when the starting surface is less than perfect. We'll now investigate whether epitaxial growth is possible at reduced substrate temperatures utilizing the assistance of the ultrasonic "agitation" to promote surface mobility. The substrate temperature is lowered to 500 °C, and 100 Å of silicon are deposited at a rate of 0.5 Å/sec. During the deposition the ultrasonic agitator is on, at low power. The resulting two-dimensional (2D) RHEED pattern shown at Fig. 8 (a) indicates a perfect epitaxial growth. The deposition is continued with 100 Å of silicon at each temperature: 450, 400 and 350 °C with deposition rate and ultrasound power the same as before. The corresponding RHEED patterns are shown in Figs. 8 (b), (c), and (d) respectively. The RHEED pattern at 450, and even 400 °C, is still showing a clear 2D structure. At 350 °C the pattern is starting to exhibit 3D features. However, please note that at 350 °C, the substrate temperature is already 200 °C lower than the temperature of 550 °C commonly used for epitaxial growth of silicon.

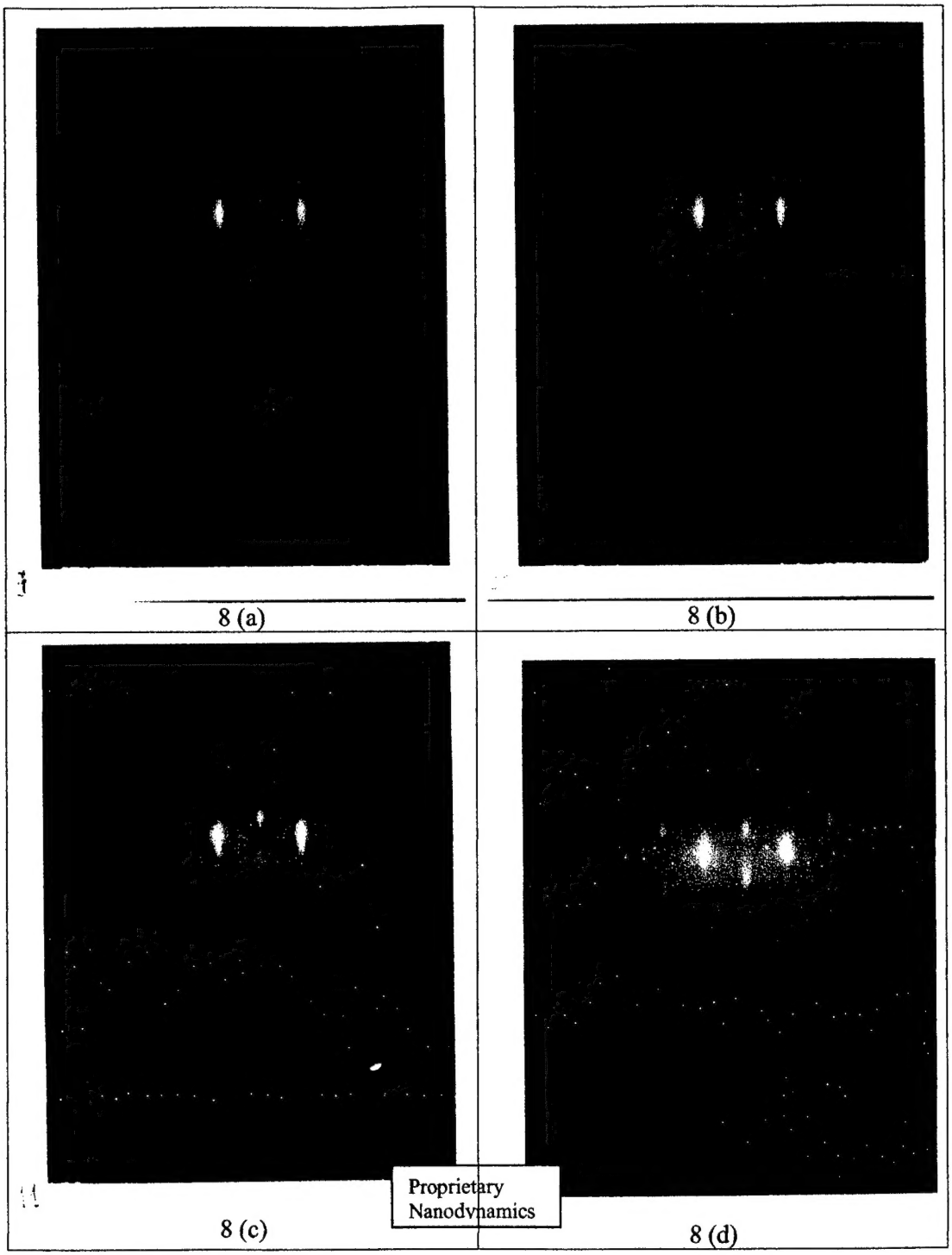


Fig. 8. Ultrasonically assisted epitaxial silicon growth at reduced temperature.
(a) Deposition at 500 °C; (b) deposition at 450 °C; (c) deposition at 400 °C; (d) deposition at 350 °C.

We wanted to investigate if we could recover the 2D epitaxial growth at 350 °C by increasing the ultrasonic field, while keeping all other deposition parameters the same. Therefore, we proceeded to increase the RF power into the ultrasonic transducer by 30% and deposit 100 Å of silicon at 350 °C and at 0.5 Å/sec. The resulting RHEED pattern is shown in Fig. 9 (a). It is evident that there is a noticeable improvement in the 2D pattern compared to the case of Fig. 8 (d). Increasing the RF power into the transducer by 60% more, and depositing an additional 100 Å of silicon at 350 °C and at 0.5 Å/sec results again in a perfect 2D structure as evidenced by the RHEED pattern shown in Fig. 9 (b). Figure 10 shows the RHEED pattern after deposition of additional 100 Å of silicon at 300 °C and 0.5 Å/sec, with the ultrasound power "on", and at the same power into the crystal as before. Please note that even at a substrate temperature of 300 °C the RHEED pattern remains 2D, as long as the deposition is assisted by the use of the ultrasound at a relatively elevated power level than previously utilized.

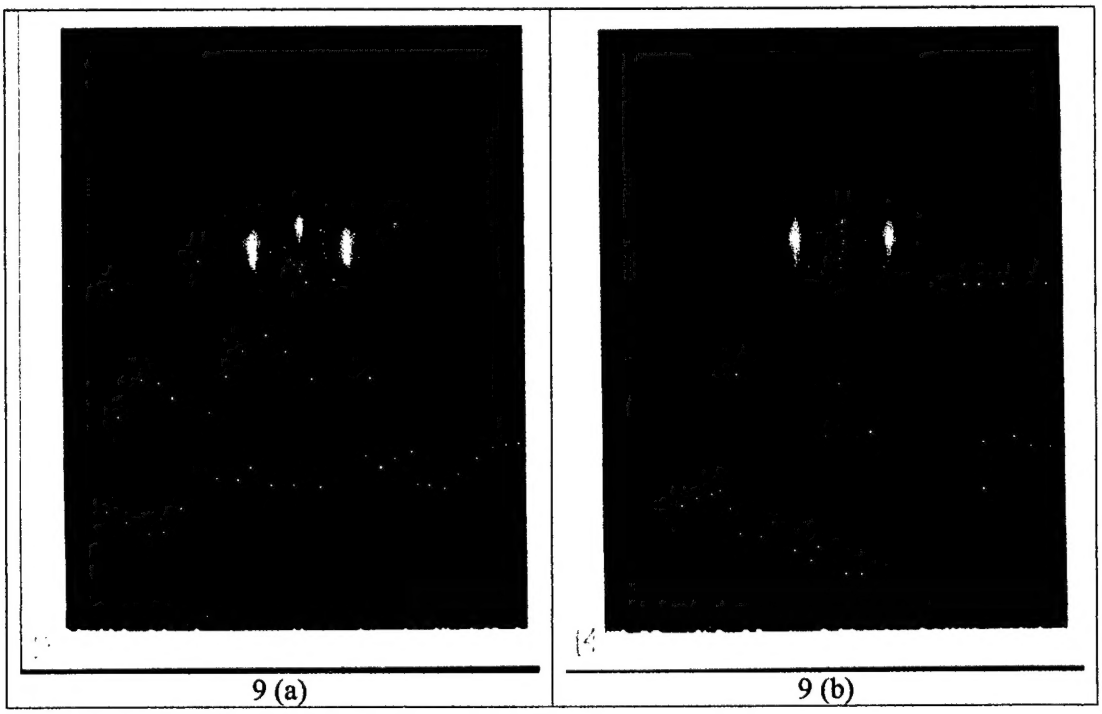


Fig. 9. (a) Additional 100 Å of silicon at 350 °C and at 0.5 Å/sec, with the power in the ultrasonic transducer increased by 30%; (b) Additional 100 Å of silicon at 350 °C and at 0.5 Å/sec, with the power in the ultrasonic transducer increased by 60%.

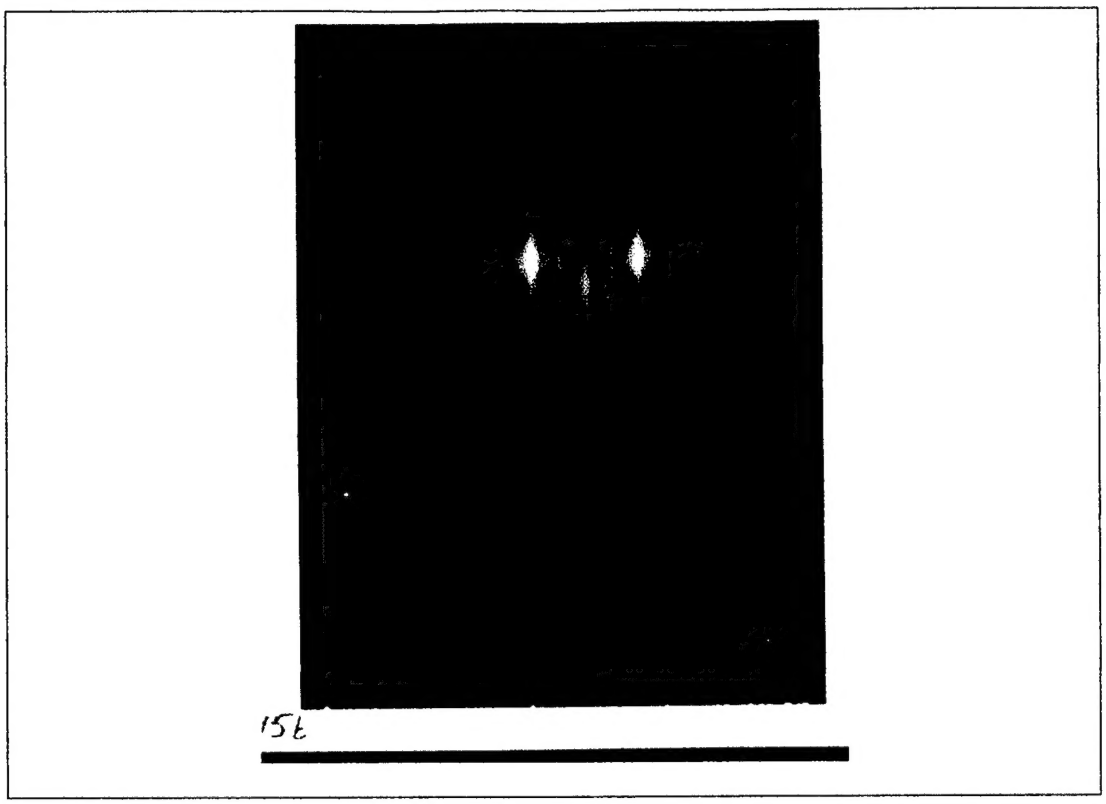


Fig. 10. Additional 100 Å of silicon at 300 °C and at 0.5 Å/sec

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5. Conclusion

During Phase I support two types of ultrasonic transducers were designed and fabricated. These transducers were utilized for ultrasonically assisted deposition of silicon under Molecular Beam Epitaxy (MBE). Epitaxial Si growth on (100) Si wafers has been observed at reduced substrate heater temperatures when accompanied by simultaneous ultrasonic agitation of the substrate during deposition.

6. References

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7. Time Chart

	3 Months	6 Months	9 Months
Equipment procurement	X		
Construction of fixtures for piezoelectric crystals	X	X	
Experiments to investigate oscillation of sample	X	X	
Adaptation of deposition systems for ultrasound experiments	X	X	
High temperature deposition		X	X
Characterization of the samples		X	X
Investigation of possible extension of the technique to more complex materials (i.e. SiC,...)			X
Reports (3 month)	X	X	
Final report			X